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Electrohydrodynamic removal of particles from drop surfaces

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A uniform electric field is used for cleaning drops of the particles they often carry on their surface. In a first step, particles migrate to either the drop's poles or equator. This is due to the presence of an electrostatic force for which an analytical expression is derived. In a second step, particles concentrated near the poles are released into the ambient liquid via tip streaming, and those near the equator are removed by stretching the drop and breaking it into several droplets. In the latter case, particles are all concentrated in a small middle daughter droplet.

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Drops immersed in another immiscible liquid often carry small particles on their surface due to the fact that when particles are present either within drops or in the ambient fluid, they are readily trapped at the interface, especially when the contact angle is around 90°, and once captured they remain so under the action of the capillary force which is much stronger than the force due to random thermal fluctuations. This ability of drops to attract particles on their surface can be used in applications such as cleaning the ambient fluid, using drops as particle carriers particularly in microfluidic devices, and stabilizing emulsions [1]. The focus of this work is on the removal of particles accumulated on drops' surfaces, which should be useful to purify drops, e.g., for the synthesis of ultra pure particles, delivering particles carried by drops once target sites have been reached and demulsifying emulsions stabilized by particles.

It was noted in [2] that even when the applied electric field is uniform, the distribution of the electric field on the surface of a drop is nonuniform, and thus a particle on or near its surface experiences a dielectrophoretic (DEP) force that causes it to move either to the equator or to one of the poles. In this study, we use the point-dipole approach to estimate the DEP force acting on a particle that causes it to migrate toward the poles or the equator. The drop is assumed to be spherical. The approach assumes that the electric field is not altered by the presence of the particle, the particle size is small compared to the length scale over which the electric field varies and the electric field gradient at the center of the particle can be used to estimate the DEP force acting on the particle [3,4]. When these assumptions are no longer valid, the exact methods based on the Maxwell stress tensor are available [4] but the extension of those to the case of particles placed a curved interface falls outside the scope of the present work.

The position of a particle within the interface is determined by the balance of the vertical forces acting on the particle, the latter consisting in our case of the capillary force (which depends among other factors on the three-phase contact angle on its surface which can change in the presence of an externally applied electric field), the electric force in the normal direction to the interface, and the particle's buoyant weight [5]. We will assume that the particle's center is at the interface but at a negligible distance outside the drop's surface, and therefore the nonuniform electric field outside the drop is used to estimate the DEP force. Here, we also wish to note that the electric field intensity inside the drop is constant, and thus, since its gradient is zero, if the particle center is assumed to be inside the drop, the DEP force on the particle, within the point-dipole approximation, will be zero.

The r and θ components of the root mean square (rms) of the electric field outside a spherical drop of radius a can be shown to be given by (see Ref. [6])

$$E_r = E_0 \cos\theta\left(1+\frac{2\beta a^3}{r^3}\right), \quad E_\theta = -E_0 \sin\theta\left(1-\frac{\beta a^3}{r^3}\right), \tag{1}$$

where E_0 is the rms value of the applied ac electric field which is assumed to be along the z direction of the spherical coordinate system, $\beta(\omega)=\mathrm{Re}(\frac{\varepsilon_d^*-\varepsilon_c^*}{\varepsilon_d^*+2\varepsilon_c^*})$ is the Clausius-Mossotti factor, and r is the distance of the particle from the drop's center. Here ε_d^* and ε_c^* are the frequency-dependent complex permittivities of the drop and the ambient fluid, respectively, and ω is the frequency of the ac field. Also, the complex permittivity $\varepsilon^*=\varepsilon-i\sigma/\omega$, where ε is the permittivity, σ is the conductivity, and $i=\sqrt{-1}$.

The DEP force acting on a particle of radius R slightly outside the surface of the drop, within the point-dipole approximation, is given by $F_{DEP}=2\pi\beta' R^3\varepsilon_0\varepsilon_c\nabla E^2$ [3,6]. Here ε_0 is the permittivity of free space, $\beta'(\omega)=\mathrm{Re}(\frac{\varepsilon_p^*-\varepsilon_c^*}{\varepsilon_p^*+2\varepsilon_c^*})$, ε_p^* is the complex permittivity of the particle, and E is the electric field magnitude:

$$E^2 = E_0^2\left[1+\cos^2\theta\left(\frac{4\beta a^3}{r^3}+\frac{4\beta^2 a^6}{r^6}\right)+\sin^2\theta\left(-\frac{2\beta a^3}{r^3}+\frac{\beta^2 a^6}{r^6}\right)\right]. \tag{2}$$

The θ component of the DEP force, which for an undeformed drop is in the tangential direction to the drop's surface, is then given by

$$F_{DEP,\theta} = -4\pi\beta' R^3 \varepsilon_0 \varepsilon_c \left[E_0^2 \cos\theta \sin\theta \left(\frac{6\beta a^3}{r^4} + \frac{3\beta^2 a^6}{r^7} \right) \right]. \quad (3)$$

Equation (3) is also valid for a dc electric field in which case E_0 denotes the electric field intensity. The force on a particle near the drop's surface can be obtained by substituting $r \approx a$, which gives

$$F_{DEP,\theta,a} = -12\pi R^3 \frac{1}{a} \varepsilon_0 \varepsilon_c E_0^2 \beta' \beta (2+\beta) \cos\theta \sin\theta. \quad (4)$$

The above expression gives the DEP force in the θ direction on a small particle near, but outside, the drop's surface. The force is zero both at the poles ($\theta = 0, \pi$) and at the equator ($\theta = \pi/2$) and maximum at $\theta = \pi/4$. Also, the force acting on a particle of a given radius increases with decreasing drop size. This implies that within the assumptions made in this work, the smaller the size of the drop, the easier it is to concentrate particles (of a given radius), a result consistent with our experimental observations.

From Eq. (4) we deduce that the sign of $\beta'\beta(2+\beta)$ determines the direction of the tangential DEP force. However, since $|\beta| \leq 1$, the factor $(2+\beta) > 0$. Thus, the sign of $\beta'\beta(2+\beta)$ is the same as that of $\beta'\beta$. Nevertheless, for $\beta < 0$ the magnitude of the factor $(2+\beta)$ is smaller than for $\beta > 0$. Thus, the DEP force is smaller in the former case. In addition, although the force is zero at both the poles and the equator, it is easy to see that the sign of $\beta'\beta$ determines the locations at which particles eventually aggregate. When $\beta'\beta > 0$ particles aggregate at the poles as they are in a state of stable equilibrium at the poles and in a state of unstable equilibrium at the equator. On the other hand, when $\beta'\beta < 0$, they aggregate at the equator where their equilibrium is stable. This result is consistent with experimental findings (see [2] and results below).

From this, for example, we may conclude that particles for which the Clausius-Mossotti factor is positive ($\beta' > 0$) aggregate at the poles if the permittivity of the drop is greater than that of the ambient fluid, and at the equator if the permittivity of the drop is smaller than that of the ambient fluid (as was noted in [2] without going through the previous analysis). It is important to note that if the fluids' and particle's conductivities are not negligible, the signs of β' and β may also depend on the frequency of the ac field. Furthermore, it is possible that the electric field induced fluid flow also causes some motion of the particles trapped on the surface of a drop. This, however, was not the case in the present experimental study.

It is noteworthy that a particle trapped on the drop's surface is in contact with both fluids instead of just the outer fluid. Expression (4) for the DEP force, which assumes that the particle's center is outside the drop, is therefore only approximate. Clearly, the Clausius-Mossotti factor β' for a particle trapped on the surface and the DEP force should depend on the permittivities and conductivities of the particle and the two fluids involved—and not just those of the outer fluid—and also on the position of the particle within the interface. The position of the contact line on the particle's surface, which determines the fraction of the particle immersed in each fluid, depends on the contact angle, the buoyant weight of the particle, and any additional force normal to the interface acting on the particle [5]. A change in the contact angle due to electrowetting can also cause the particle to move in the direction normal to the interface to satisfy the new contact angle requirement [7]. In addition, the electric force normal to the interface can also change the particle's position [8]. It is, however, beyond the scope of the present investigation to include these factors in the analysis presented above.

So far, we have assumed that the drop remains spherical. However, a drop subjected to a uniform electric field deforms due to the nonuniformity of the electric stress distribution on its surface. Its deformed shape is determined by the balance of the surface tension force, which tends to make the drop spherical, and the force due to the electric stress [9]. Furthermore, there is a critical electric field intensity above which the drop undergoes tip streaming or breaks [9,10]. In this study we show that tip streaming can be exploited to remove particles accumulated near the poles and drop breaking can be used to remove particles accumulated near the equator. Our experiments reported below show that when the distance between the electrodes is about three times the drop diameter, or smaller, the drop bridges the gap between the electrodes and then breaks in the middle (see Fig. 1). On the other hand, the drop tip streams when this distance is about five times the drop diameter or larger. The critical electric Weber number ($\mathrm{We} = a\varepsilon_0\varepsilon_c E_0^2 \beta^2 / \gamma$, where γ is the interfacial tension) that is the ratio of the electric and capillary forces, at which the drops tip streamed or bridged the gap between the electrodes was approximately 0.085. For a given system (fluids, particles, and experimental setup), this value defines the minimum electric field (and thus voltage difference) needed. In a smaller device, the drop bridges the gap because the electric field intensity and the electric stress in the region between the electrodes and the drop's surface are enhanced due to the smaller size of the gap, as shown by the direct numerical simulation results reported in Fig. 1 (for the details of the computational approach see [11,12]).

Experiments were conducted in a device with a rectangular cross section in which the electrodes were mounted on the side walls. The distance between the electrodes was 6.5 mm, the depth 6.5 mm, and the length 41 mm. The depth of the ambient fluid in the device was approximately 5.5 mm. To make the bottom surface hydrophobic, the latter was covered by a layer of polytetrafluoroethylene (PTFE). A variable frequency ac signal generator (BK Precision Model 4010A) was used along with a high voltage amplifier (Trek Model 5/80) to apply voltages to the electrodes. The motion or deformation was recorded using a digital color camera connected to a Nikon Metallurgical MEC600 microscope.

The millipore water drops containing particles on their surfaces were formed in corn oil using the procedure described in [2]. The dielectric constant of millipore water was 80.0, and its conductivity was 5.50×10^6 pS m^{-1}, and the values for corn oil were 2.87 and 32.0 pS m^{-1}. The densities of water and corn oil were 1.00 and 0.92 g/cm^3, respectively. Since the density of corn oil was slightly smaller, the drops reached the bottom of the device but did not wet the

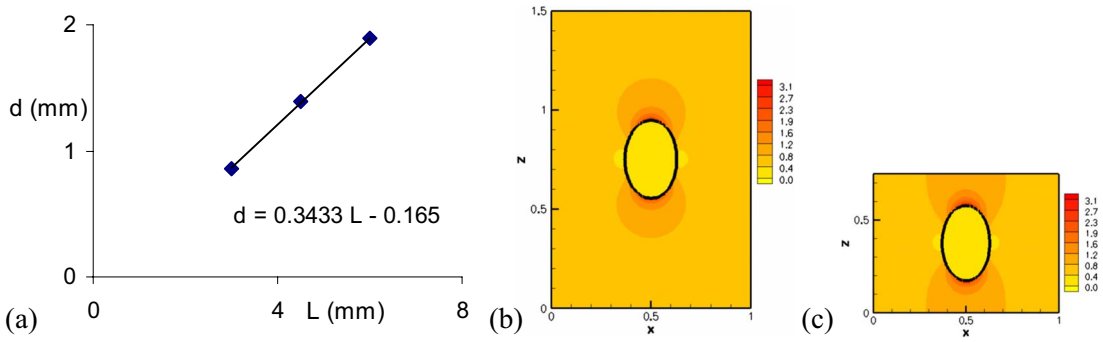

FIG. 1. (Color online) The diameter d of the smallest water drop that bridged the gap between the electrodes in our experiments is plotted as a function of the distance L between the electrodes, showing a linear dependence with L (with the best linear fit shown here). Tip streaming occurred for the drops that were of the smaller diameter. The drops were immersed in corn oil and the electric field frequency was 1 kHz. Figures (b) and (c) show that the presence of a drop makes the electric field distribution nonuniform and that the electric field strength in the gap between the drop and the electrode increases with decreasing gap. The electrodes are mounted on the upper and lower walls of the figure. The electric field in the presence of a drop is computed numerically using the approach described in [11,12]. The drop permittivity is 30 times larger than that of the ambient fluid and the electric Weber number is 0.9. In (b) the distance between the electrodes is five times the drop diameter and in (c) it is 2.5 times the drop diameter. The intensity of the applied uniform electric field (and that of the shown isovalues) in (b) and (c) is the same. Notice that in the smaller device (c) the electric field intensity in the region between the electrodes and the drop is greater; this results in an increase in the electric stress causing the drop to bridge the gap.

bottom surface which remained covered with corn oil since it was hydrophobic. The diameter of the particles used in our experiments was between $1-70$ μm, and so we were able to visually monitor their motion. The dielectric constant of extendo spheres was 4.5 and that of polystyrene particles was 2.5. Furthermore, the drop size was such that the particle diameter was at least an order of magnitude smaller than that of the drop. The buoyant weight of the particles, however, was non-negligible and therefore the latter collected either at the top or the bottom surface of the drop, depending on their density compared to that of the liquids.

A two-step procedure was used for cleaning drops of the particles trapped on their surfaces. In the first step, an electric field of sufficiently large intensity was used to concentrate particles either at the drop's poles or at its equator. This, as noted earlier, is due to the fact that even though the applied electric field is uniform, it becomes nonuniform on and near the drop's surface if the electric permittivity of the drop is different from that of the ambient fluid. The resulting DEP force causes particles to move toward the regions of either high or low electric field strength, while they remain trapped on the drop's surface.

Figure 2 shows that extendo spheres on the surface of a water drop migrate toward the poles and aggregate there. Since the drop's permittivity is larger than that of the ambient fluid, the electric field near the equator is smaller than the imposed uniform electric field, and near the poles it is larger (see Fig. 1). This shows that extendo spheres undergo positive dielectrophoresis since $\beta' > 0$. For the same drop-ambient fluid combination, Fig. 3 shows that polystyrene particles trapped on the drop's surface migrate and collect near the equator. Since the electric field strength at the equator is locally minimal, polystyrene particles for which $\beta' < 0$ undergo negative dielectrophoresis.

In the second step, the electric field intensity was increased further to remove these aggregated particles from the drop. To remove particles aggregated near the poles, a tip-streaming mechanism was used. Figure 2 shows that for a sufficiently strong electric field the water drop develops conical ends (also called Taylor cones [9,10]) and particles concentrated at the poles eject due to tip streaming, thus leaving the drop free of particles. For a water drop suspended in corn oil, the electric field caused tip streaming when the

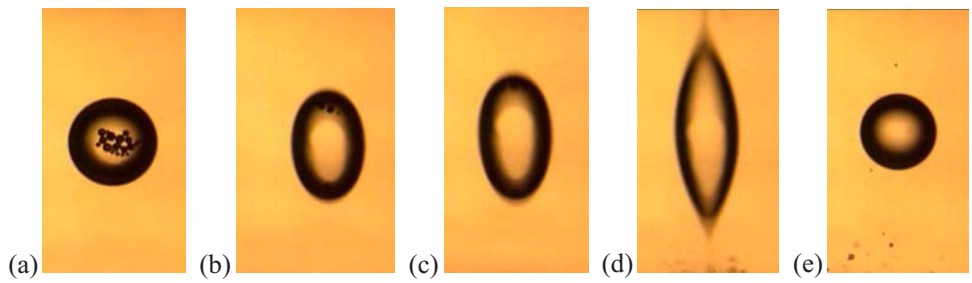

FIG. 2. (Color online) Removal of extendo spheres from a water drop immersed in corn oil. The initial drop diameter is 844.6 μm. The mean diameter of extendo spheres is 55 μm and the dielectric constant is 4.5. The distance between the electrodes mounted on the upper and lower walls of the figure (side walls of the device) is 6.5 mm and the voltage applied is (a) 0, (b) 3.2 kV, (c) 3.6 kV, (d) 3.95 kV, and (e) 0, all at 100 Hz. The various stages are the following: (a) particles are distributed quasiuniformly on the drop's top surface; (b) particles begin to cluster at the poles; (c) the drop elongates; (d) the drop shape at the poles is conical and all particles have been ejected out; (e) the drop is now clean and spherical.

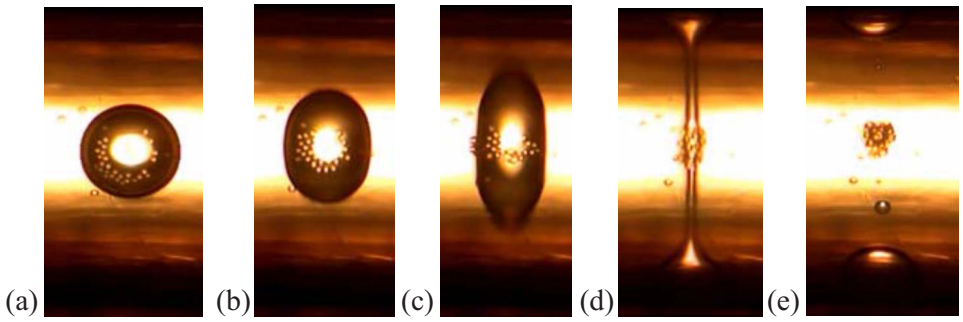

FIG. 3. (Color online) Removal of polystyrene spheres from a water drop immersed in corn oil. The drop diameter is 932.6 μm. The mean diameter of polystyrene spheres is 70.0 μm and their dielectric constant is 2.5. The distance between electrodes is 2.65 mm. The applied voltage is (a) 0, (b) 1.4 kV, (c) 1.6 kV, (d) 1.8 kV, and (e) 0 at 1 kHz. In (b) and (c) particles move toward the equator and collect in a ring shaped region around the equator. In (d) particles remain at the equator while the drop stretches and breaks into two clean drops, leaving particles in a small droplet (of high particle concentration) in the middle as can be seen in (e). Notice that there are some particles outside the drop which remained outside throughout this experiment.

distance between the electrodes was ~5 times the drop diameter or larger.

To remove particles aggregated near the equator, we used a device for which the gap between the electrodes was approximately three times the drop diameter. In this case, the drop bridged the gap but did not tip stream and then broke in the middle because of the thinning of the filament (see Fig. 3). The middle droplet was formed because all of the fluid contained in the filament was not transferred to the two main droplets. The middle droplet contained all the particles, and the two larger sized droplets were free of particles. The breakup near the middle occurred when the filament diameter became smaller than the thickness of the region occupied by the particles, and the size of the middle droplet was found to increase with increasing concentration of particles.

In this work, we have confirmed that an externally applied uniform electric field can be used to manipulate particles trapped on the surface of drops leading to their concentration near the poles or the equator of the drop and obtained an analytical expression for the electrostatic force acting on the particles. It was further shown that these concentrated particles can then be removed by increasing the electric field intensity. The technique offers a way for releasing small particles (including nanoparticles) from drops to the ambient fluid if the liquids are judiciously selected so that particles aggregate near the poles. It obviously can work only if the liquids involved are such that an electric field of sufficiently large intensity induces tip streaming. If, on the other hand, liquids are such that particles cluster near the equator, the drop stretches and, if placed in a small device, then bridges the gap between the electrodes. It then breaks into several daughter droplets, with the middle one containing all of the particles. In addition, it was shown computationally that the drop bridges the gap between the electrodes due to the electric stress enhancement that occurs when the gap between the drop and an electrode is of the order of the drop size.

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